ज़िंदगी मे सफलता पाने की चाहत सभी को होती है पर ये मिलती उन्ही को है जिनके इरादों मे जान होती है ।

CSIR NET – Life Science

Unit 1: Biochemistry

06 **Carbohydrates**

Points to be covered in this Lecture

- Monosaccharides
- Stereo-isomerism
- Optical Activity
- Oligosaccharides
- Reducing Sugars
- Starch and Glycogen
- Cellulose, Chitin, Pectin
- Hetero-polysaccharides

carbohydrates !

Carbohydrates

Most **abundant** biomolecule ✓

Compounds of C, H and O ✓

General formula: $C_nH_{2n}O_n$ where 'n' is 3 or more ✓

C H O
1 : 2 : 1

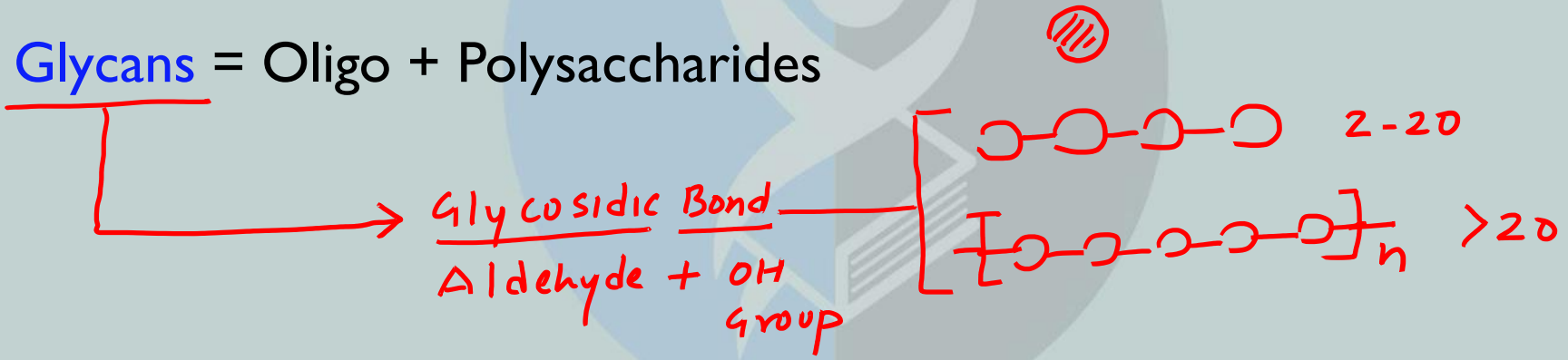
Hydrated form of Carbon: $C_n (H_2O)_n$

Chemically: Poly hydroxy aldehydes (aldoses eg. Glucose) or
Poly hydroxy ketones (ketoses eg Fructose)

Carbohydrates are divided into 3 main classes

- ☐ **Monosaccharides** (Simple sugars – 3 to 9 Carbons)
- ☐ **Oligosaccharides** (Contains 2 to 20 sugar residue)
- ☐ **Polysaccharides** (Contains over 20 sugar residue)

Glycans = Oligo + Polysaccharides



1. MONOSACCHARIDES : → monomers for glycans

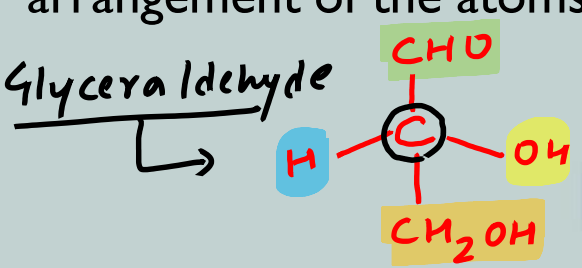
Single sugar unit which cannot be further hydrolyzed into still smaller carbohydrates

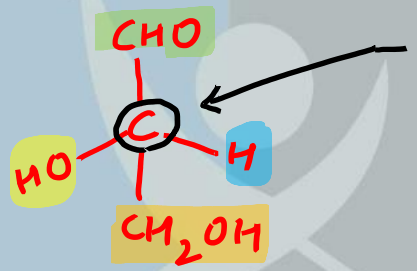
- Triose – 3C
- Tetrose – 4C
- Pentose – 5C
- Hexose – 6C
- Heptose – 7C

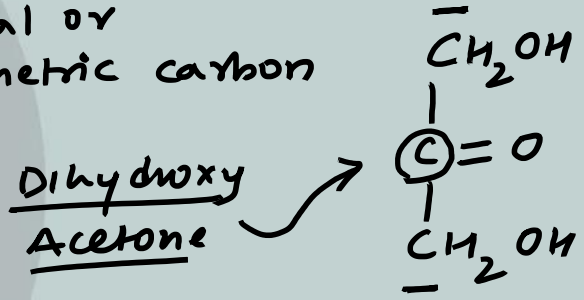
		Aldoses	Ketoses
3C	Triose	Glyceraldehyde	Dihydroxy acetone
4C	Tetrose	Erythrose Threose	Erythrulose
5C	Pentose	Ribose Xylose Arabinose Lyxose	Ribulose xylulose
6C	Hexose	Glucose (Dextrose) Galactose Mannose	Fructose (Laevulose)

Stereoisomers:

Have the same molecular formula and connectivity, but a different 3-D spatial arrangement of the atoms.

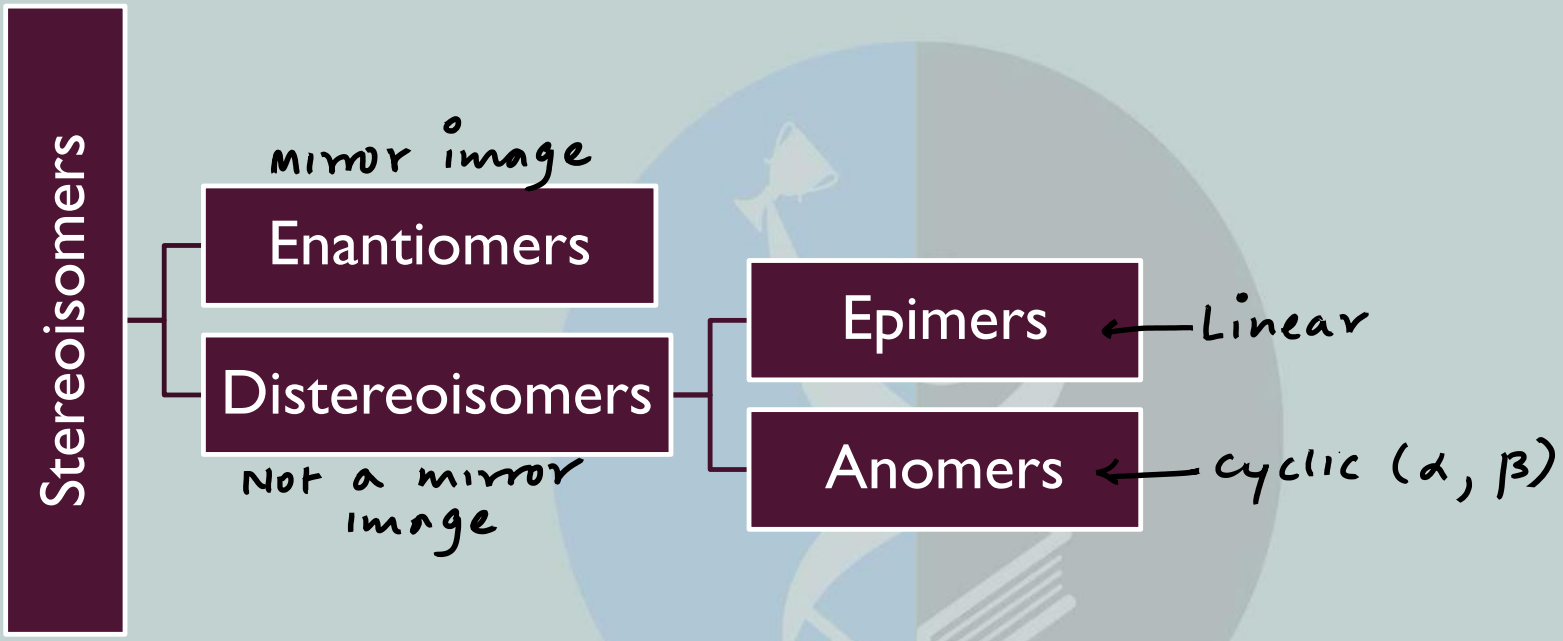






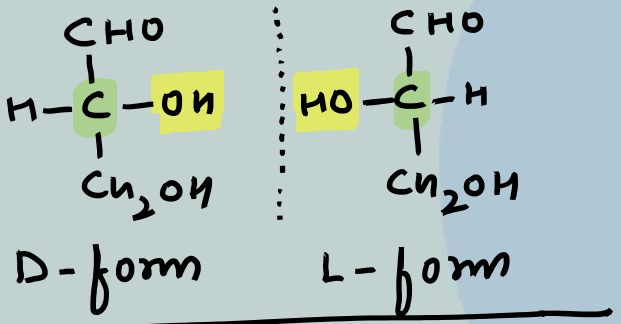
A molecule with '*n*' chiral centers = 2^n stereoisomers.

	Aldehyde	Stereoisomer	Ketone	Stereoisomer
Triose(3C)	n = 1	2	n = 0	1
Tetrose(4C)	n = 2	4	n = 1	2
Pentose(5C)	n = 3	8	n = 2	4
Hexose (6C)	n = 4	16	n = 3	8


Stereoisomers
Enantiomers
mirror image
Distereoisomers
Not a mirror image
Epimers
Linear
Anomers
cyclic (α, β)

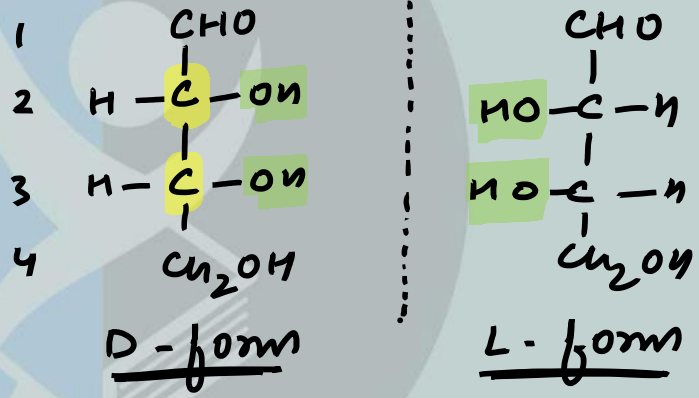
Enantiomers:

D and L forms of a monosaccharide are non-superimposable mirror images. (R & S)



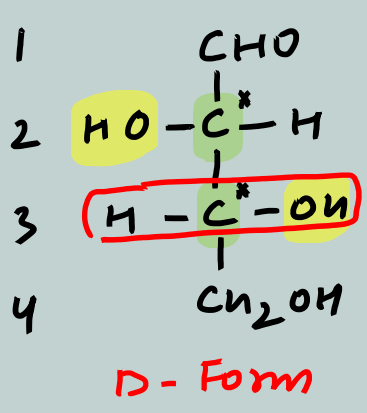
- Absolute configuration

Glyceraldehyde

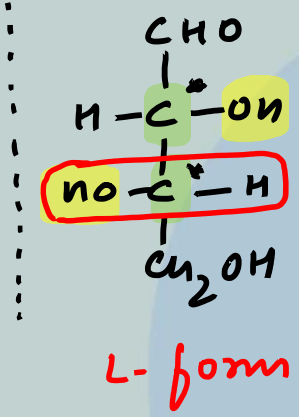


Erythrose

When more than one chiral center is present : compare last chiral carbon with D or L- form of Glyceraldehyde

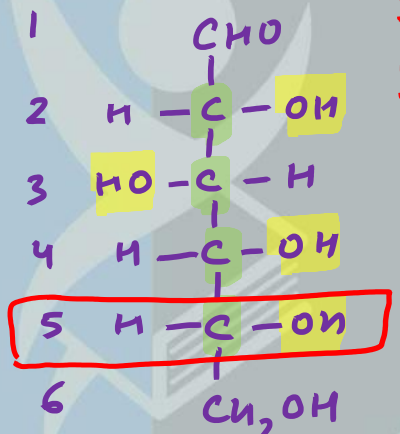


D- Form

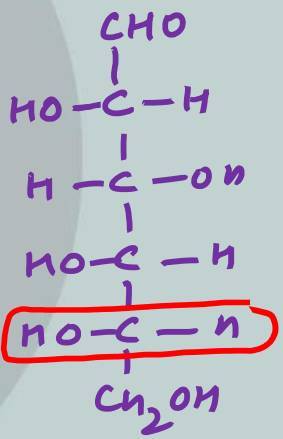


L- form

Threose



D- form



L- form

Glucose

Most of Sugar in biological system are D-form

L-form → Rare

↓ L-form (unstable) $\xrightarrow{\Delta G^\circ = -ve}$ D-form (stable) ↑

→ steric hindrance = ↑

D-form (stable) ↓

- occurance = ↑
- Enzymes & transporter will evolve for their utilization

Energy = ↑ unstable

↓ Heat Relase (Exothermic)

Energy = ↓ (stable)

ΔG = Decrease (-ve)

D and L indicate the configuration of an asymmetric carbon,
They ***do not indicate rotation of plane polarized light***

D-Glucose = +52 (Dextrorotatory)
D-Fructose = −92 (Laevorotatory)

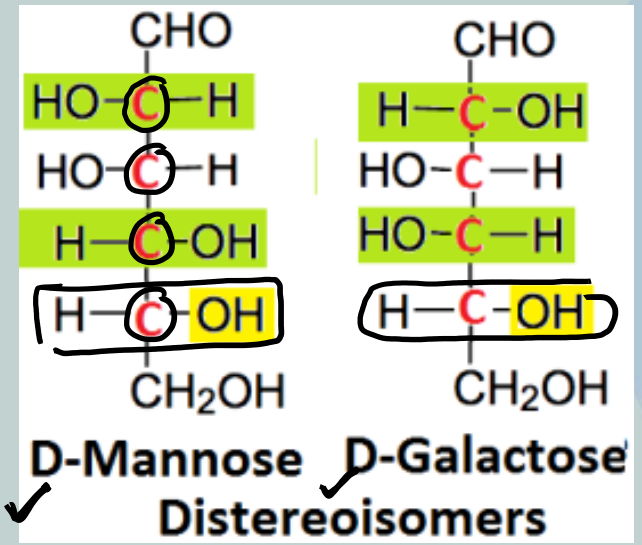
L-Glucose = −52°
L-Fructose = +92°

Dextrorotatory : d or + (not D)
Laevorotatory : l or − (not L)

Enantiomers have the same physical properties, except for the direction in which they rotate polarized light

Distereo-isomers:

Stereoisomers of a compound have different configurations at one or more (but not all) of the equivalent (related) stereo-centers (chiral carbon)

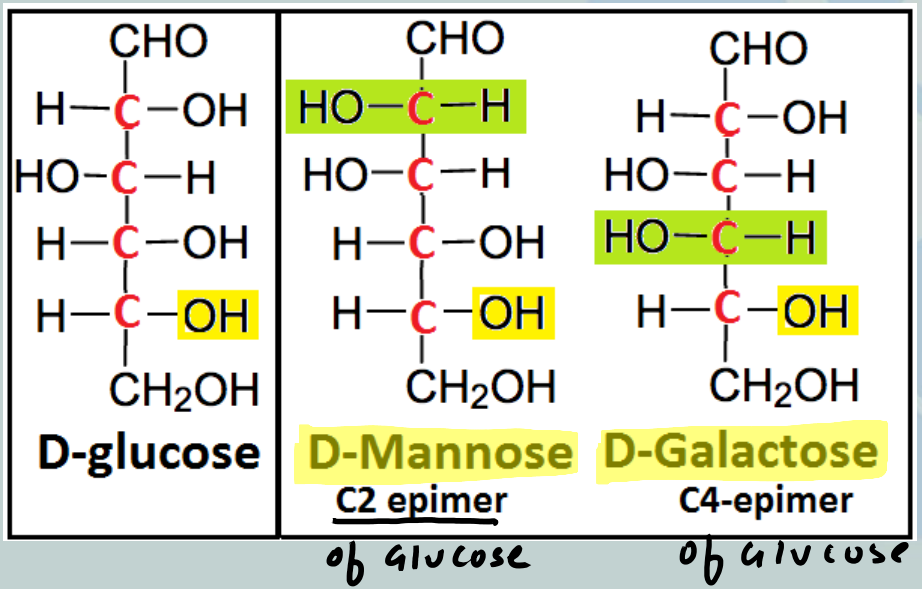


1
2 ← change in OH position
3 No change
4 ← change
5 No chang
6

If change is only at 1 place → Epimer
else simply referred as distereoisomer

Epimers are distereoisomers that differ in configuration of only one asymmetric carbon of enantiomers or diastereomers.

Example, D-mannose is C-2 epimers and D-galactose is C-4 epimers of glucose



Glucose & Mannose : C_2 epimer
Glucose & Galactose : C_4 epimer

Also Distereoisomer
Also stereoisomer

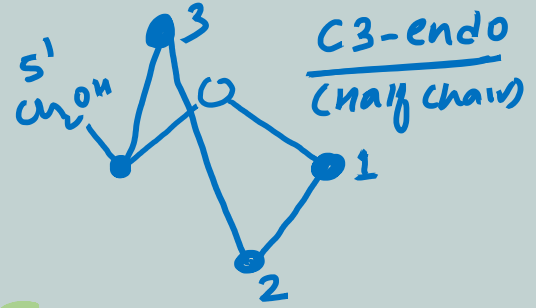
D-Mannose & D-Galactose

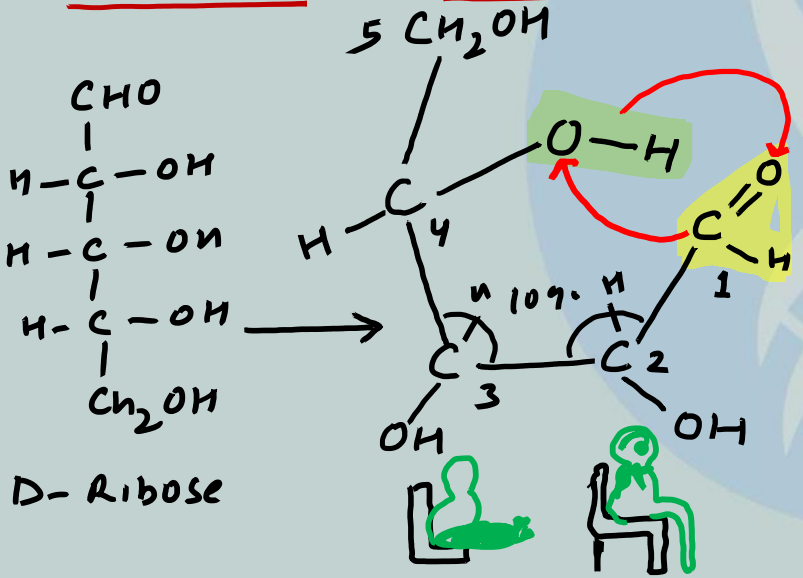
- Change at carbon 2 & carbon 4
- They are not epimer but they are distereoisomer

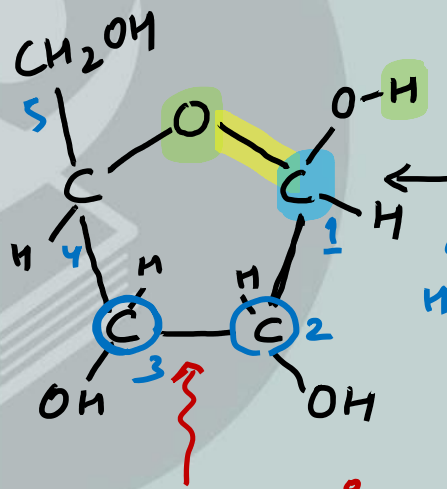
Furanose ring structure : Reactive aldehyde (Ketone) and OH group

Hemi-acetal (Hemi Ketal)

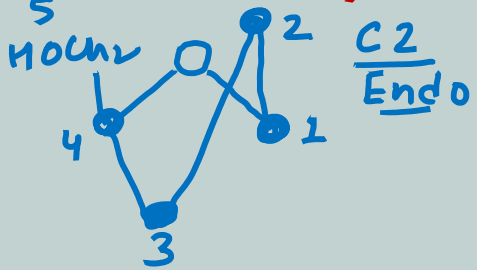
- 5 Membered Ring - 4 carbon and 1 oxygen
- Formed by Pentose aldehydes and hexose ketones
- Ring is not planar – Half chair form



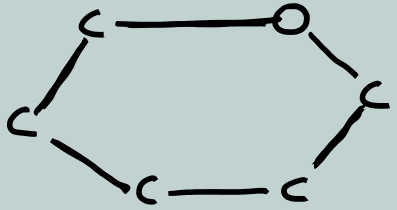




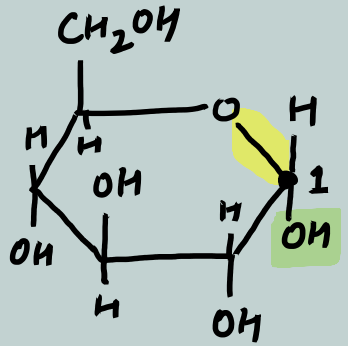
Hemi-Acetal Carbon (C1)



Pyranose ring structures

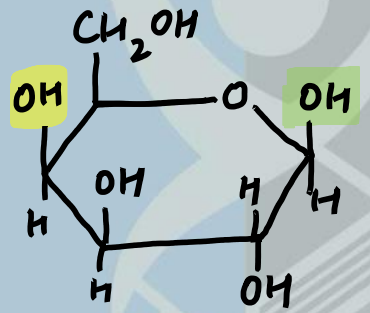


- 6 Membered Ring - 5 carbon and 1 oxygen
- Formed by Hexose aldehydes and hexose ketones (unstable)
- Ring is not planar – Chair form



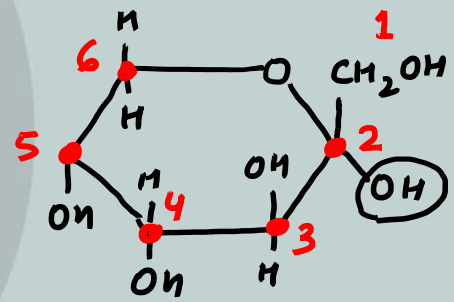
D - Glucose

α - D - Glucopyranose



β - D - Galactose

β - D - Galacto pyranose

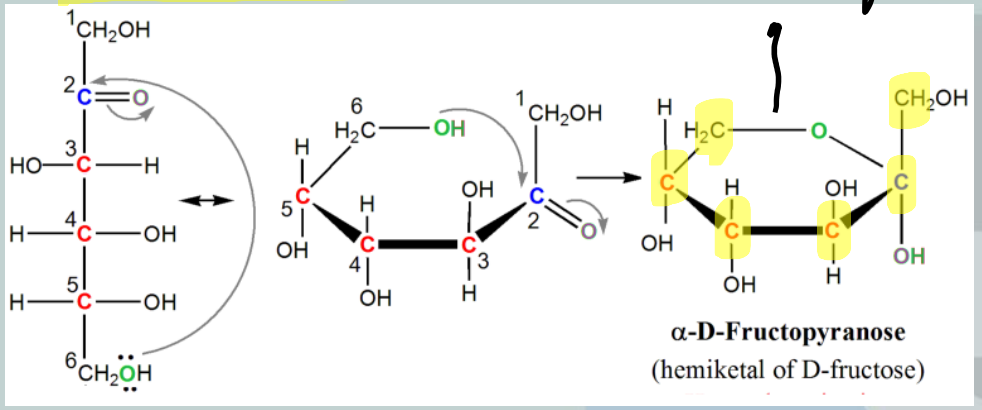


α - D - Fructose

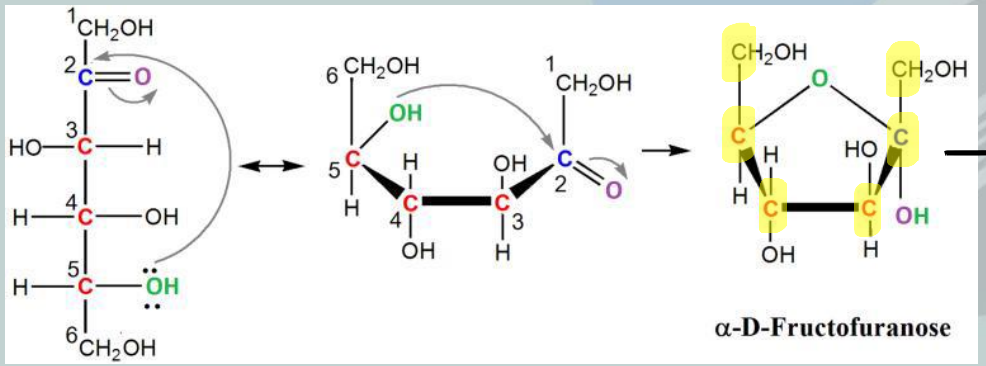
α - D - fructopyranose (unstable)

- sweetest sugar

Fructo-pyranose



Fructo-furanose



half chair

Chain form (Linear)

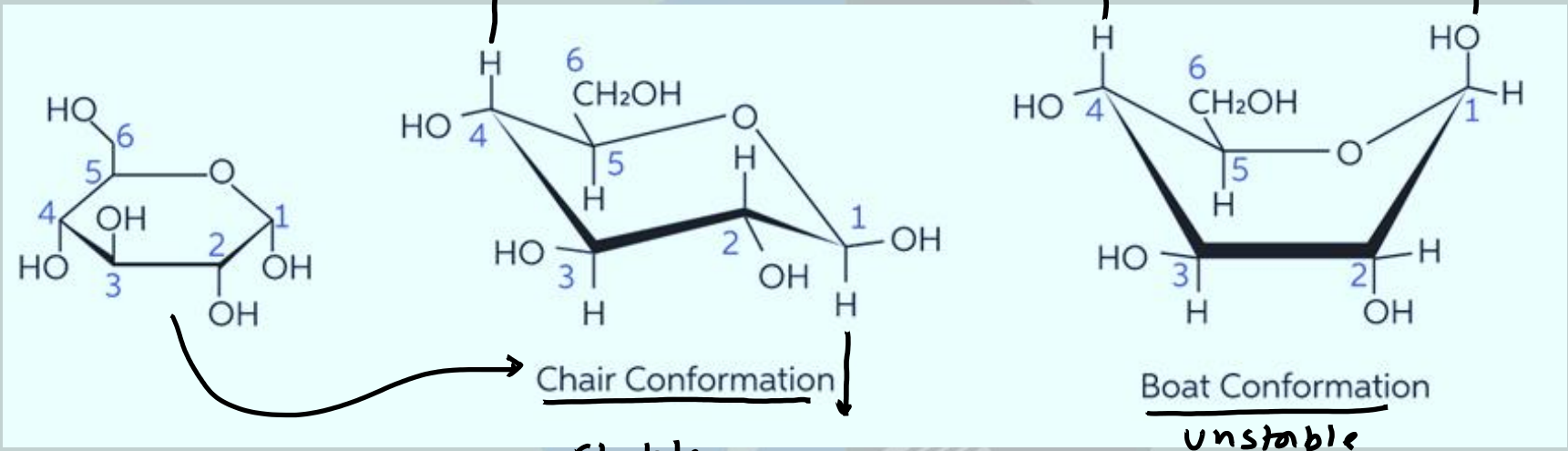
Ring form

fructopyranose
- unstable
- sweetest

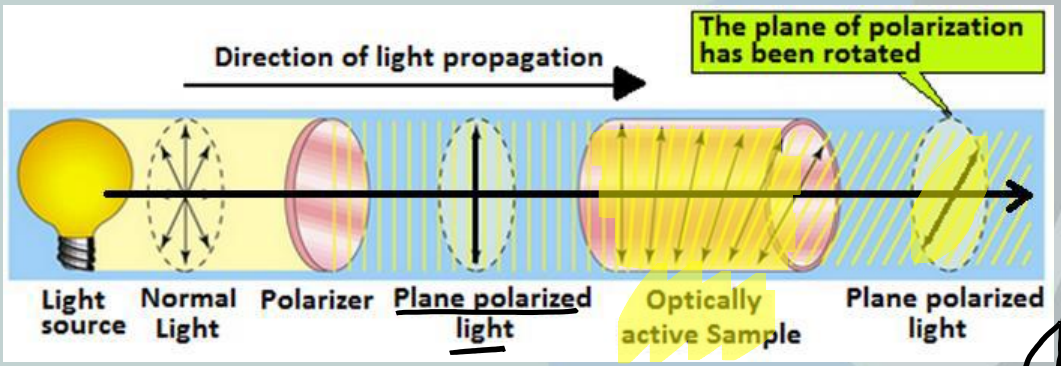
ΔG° = -ve

fructofuranose
- stable
- not much sweet

Chair form is more stable as compare to boat form



Optical Activity : molecule must have atleast one chiral carbon.



- all carbohydrates are optically active except dihydroxy acetone (3C-Ketone)

β-D-Glucose = +18.7°
α-D-Glucose = +112.2°
D-Glucose (α+β) = +52.7°

D-fructose (α+β) = −92°

Sucrose = +66°

✓ **Dextrorotatory** (+); or to the left, **levorotatory** (−)

Racemic mixtures

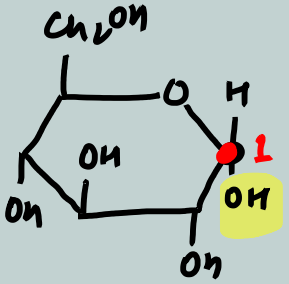
→ D-Glucose + L-Glucose = No net optical rotation
+52° −52°

Anomers: α, β

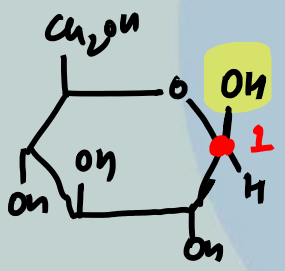
Di-stereoisomers of cyclic forms of sugars differing in the configuration at the **anomeric carbon.**

• Hemi-acetal carbon.

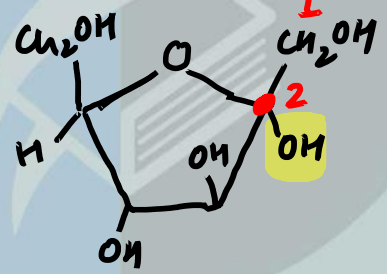
C-1 atom of an aldose or the C-2 atom of a 2-ketose. → OH-group down the plane : α-anomer
OH-group above plane : β-anomer



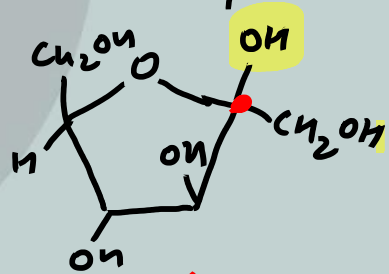
α-D-Glucose



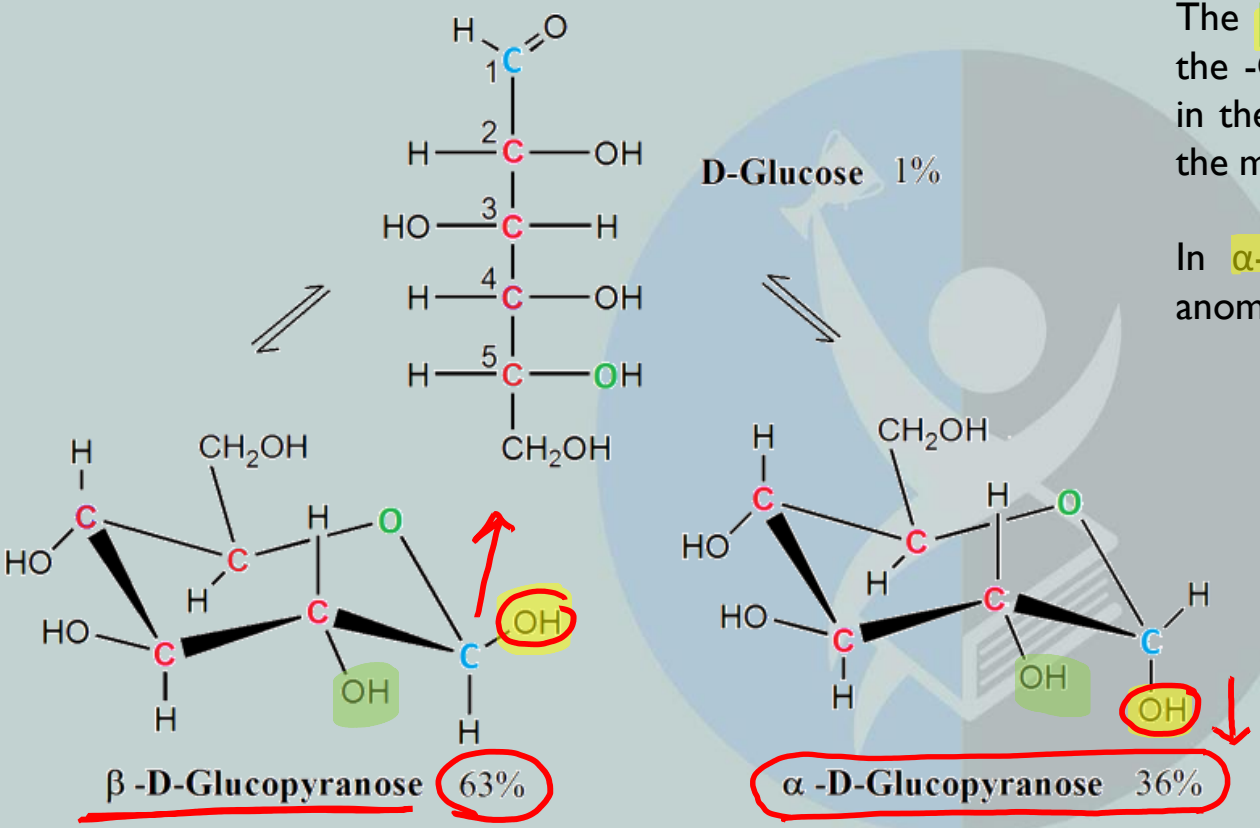
β-D-Glucose



α-D-fructose



β-D-fructose



The β-D-glucose predominates, because the -OH group of the anomeric carbon is in the more stable *equatorial position* of the more stable chair structure.

In α-D-glucose, the -OH group on the anomeric carbon is *axial.*

α-D-Glucose 1 ⇌ β-D-Glucose 2

Mutarotation: α ⇌ β-anomer

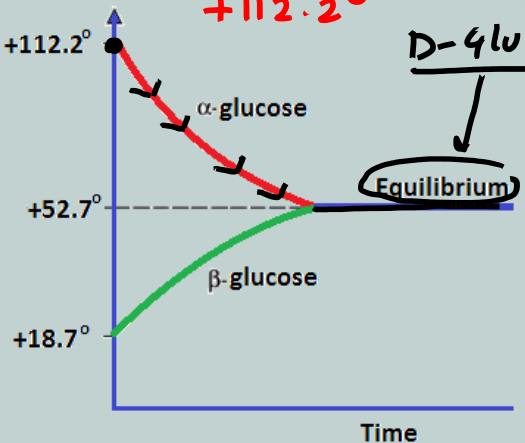
α–D–(+)–glucose ⇌ D–(+)–glucose ⇌ β–D–(+)–glucose

+112.2° +18.7

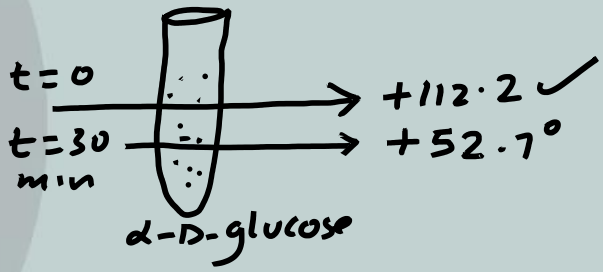
α ⇌ β

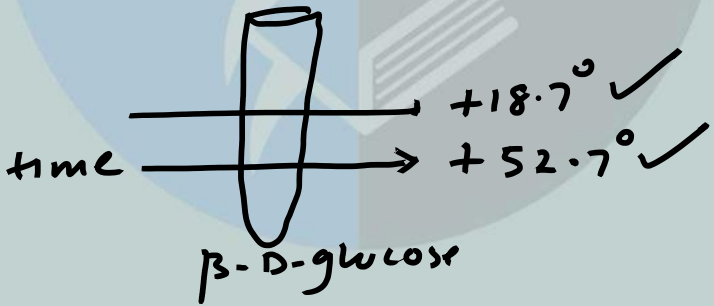
36% 63%

+112.2° +18.7



D-glucose (α + β) = +52.7°

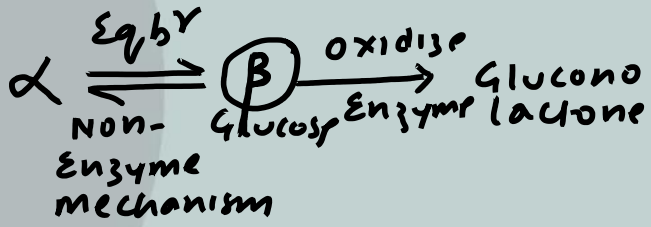




Apply Your Mind:

The enzyme glucose oxidase isolated from the mold *Penicillium notatum* catalyzes the oxidation of β-D-glucose to D-glucono-δ-lactone. This enzyme is highly specific for the β anomer of glucose and does not affect α anomer. In spite of this specificity, the reaction catalyzed by glucose oxidase is commonly used in a clinical assay for total blood glucose?

(1) Only 50 % D-glucose sugar will be monitored
(2) Only 66 % glucose sugar will be assayed
(3) Only 33 % glucose sugar will be assayed
(4) Almost total glucose will be assayed as rate of mutarotation is high.



OLIGOSACCHARIDES:

The sugars with limited numbers (2-20) of monosaccharides are called **oligosaccharides**.

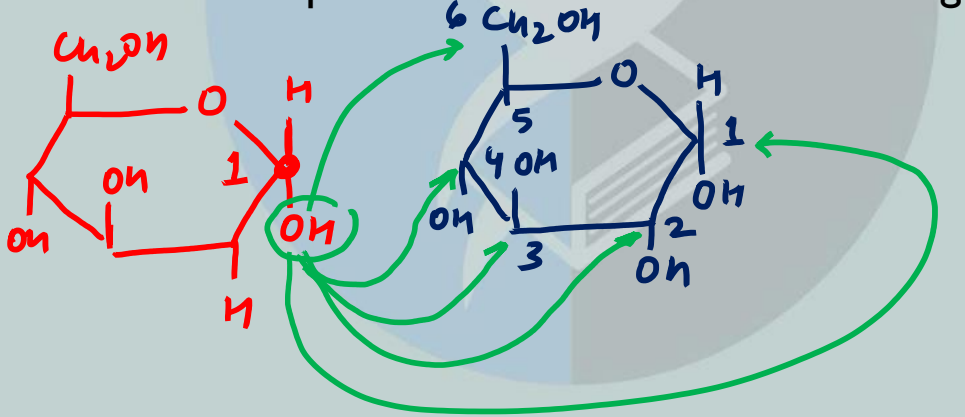
Disaccharide (2 sugars)

These include trisaccharides, tetra saccharides, hexasaccharides, heptasaccharides etc.

At least from one side anomeric position carbon is involved in O-glycosidic bond

C1 : Aldehyde
C2 : Ketone

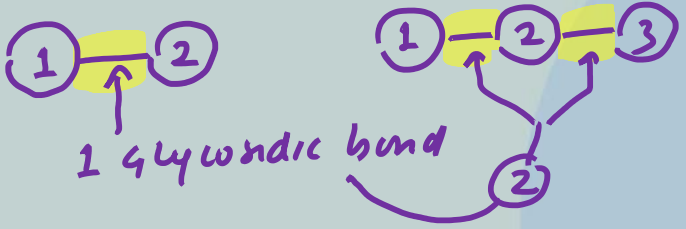
α β form

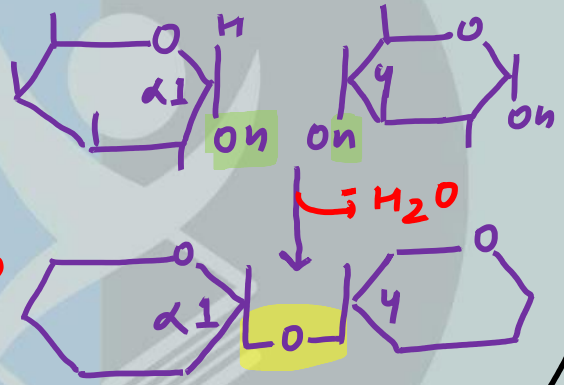


α1 → 2 β1 →
1 → 2
2 → 3
1 → 4
1 → 6

Molecular weight of oligosaccharide

Linear oligosaccharide : Number of glycosidic bond is 1 less than number of sugar residues. H_2O (18 Dalton) is released for every glycosidic bond.





- 5 glucose (180 D) are linked in linear chain. Molecular wt ?

(5 × glucose) − (4 × water)

(5 × 180) − (4 × 18)

= (900 − 72) ✓

= 828 Dalton

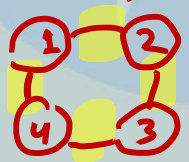
(4 × glucose) − (4 × H_2O)

= (4 × 180) − (4 × 18)

= 720 − 72

= 648 Dalton

Cyclic oligopeptide



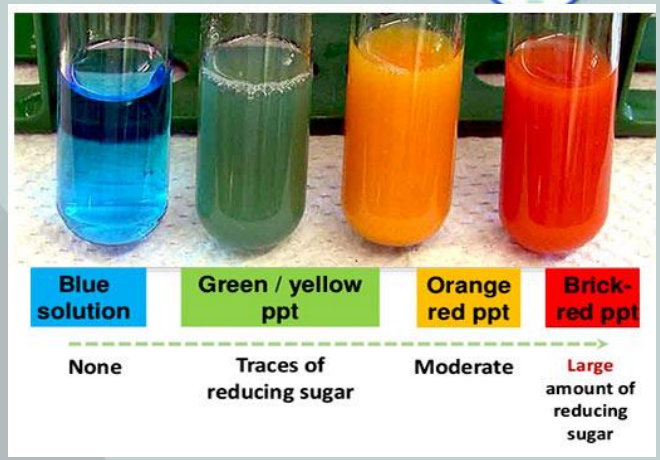
Number of H_2O molecule eliminated will be equal to number of sugar residues.

Reducing Sugars:

$Cu^{2+} \xrightarrow{e^-} Cu^{+}$ (Red)

A free aldehyde group or a free ketone group.

Benedict's reagent (Cu^{2+} in aqueous sodium citrate)
Fehling's solution (Cu^{2+} in aqueous sodium tartrate)



Reduces copper(II) ions to copper(I): forms a brick red copper(I) oxide precipitate.

colored crystals

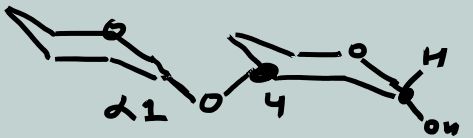
Reducing sugars also forms osazones with phenyl hydrazine

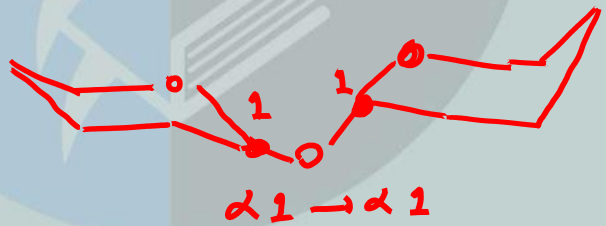
Tollens' reagent ($AgNO_3$): Silver mirror

All monosaccharides are reducing sugars, along with some disaccharides such as lactose, maltose, cellobiose.

Example	Unit 1	Unit 2	Bond	Reducing Sugar
Malotose	Glucose	Glucose	α(1→4)	Yes
Lactose	Galactose	Glucose	β(1→4)	Yes
Lactulose	Galactose	Fructose	β(1→4)	Yes
Cellobiose	Glucose	Glucose	β(1→4)	Yes
Sucrose	Glucose	Fructose	α(1→2)β	No
Trehalose	Glucose	Glucose	α(1→1)α	No

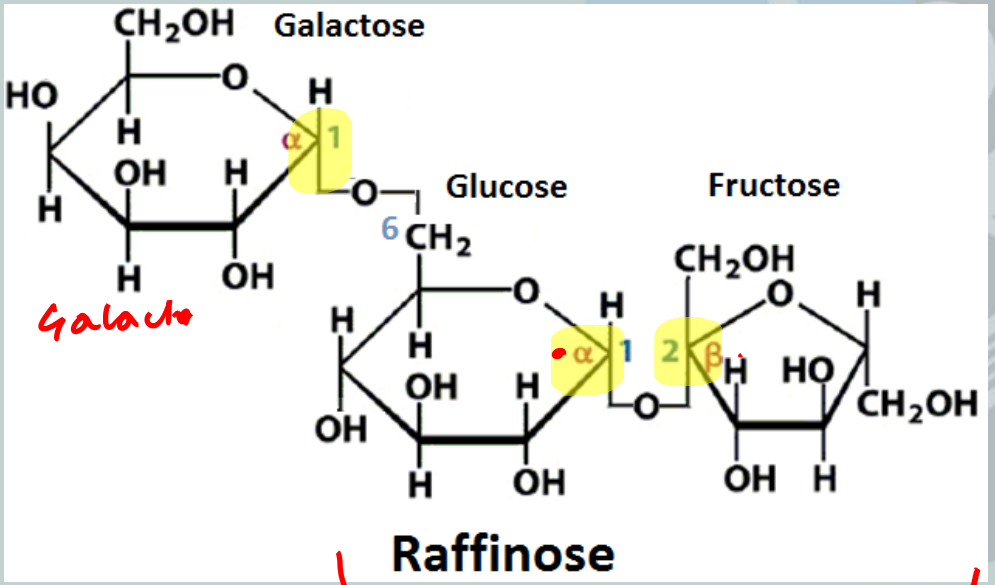
Gentobiose → Glucose Glucose β (1→6) Yes





Higher oligosaccharides:

Raffinose is a tri-saccharides composed of galactose α(1→6) glucose β(1→2) fructose.



← Non-Reducing sugar

Galacto

Sucrose

POLYSACCHARIDES:

1. **Homopolysaccharides:** single repeating sugar
2. **Heteropolysaccharide:** more than one type of sugar is repeated.

Polysaccharides

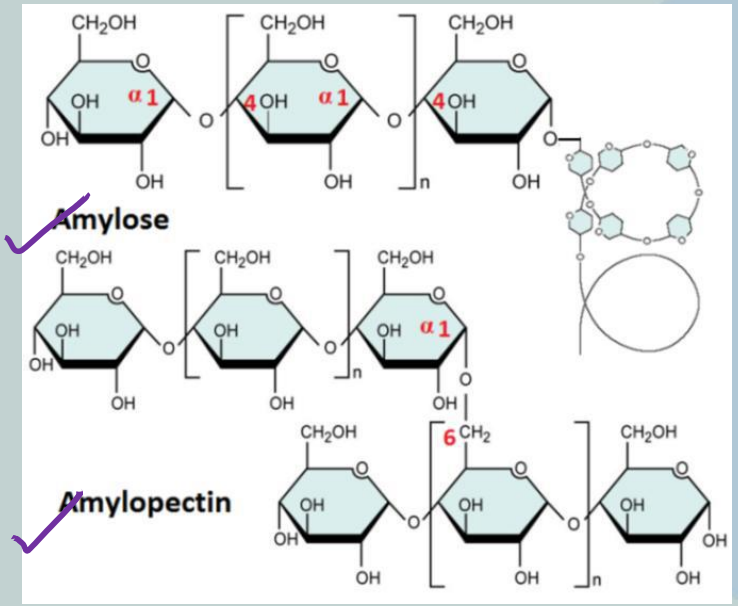
1. Energy storage : 4 K cal/g → Starch, Glycogen, Inulin

2. Structural Role
   - Cellulose, Hemicellulose
   - Pectin
   - Chitin
   - Heteropolysaccharides – Dermatan
     Keratan etc.

Storage polysaccharide

Starch: Energy storage form in plants

- Homopolymer of D-glucose



Starch

Amylose
- Simple starch
- $\alpha 1 \rightarrow 4$

Amylopectin
- Branched starch
- $\alpha 1 \rightarrow 4$ and $\alpha 1 \rightarrow 6$ bond (25-30 residue)

- Structure : Helical
- Stabilized by Intrachain H-bonding
- Synthesis : chloroplast,
- Storage : chloroplast, Leucoplast (amyloplast)

Glycogen: Animal starch

↳ Animals, Fungi, Bacteria: energy storage form

- Similar to amylopectin.
  - → α1→4
  - → α1→6 (after 9-12 residue)
- Helical structure
- Intra-chain H-bonding
- Synthesis & storage: cytosol of liver & muscles of animals
- Homo-polymer of D-glucose

Structural polysaccharide

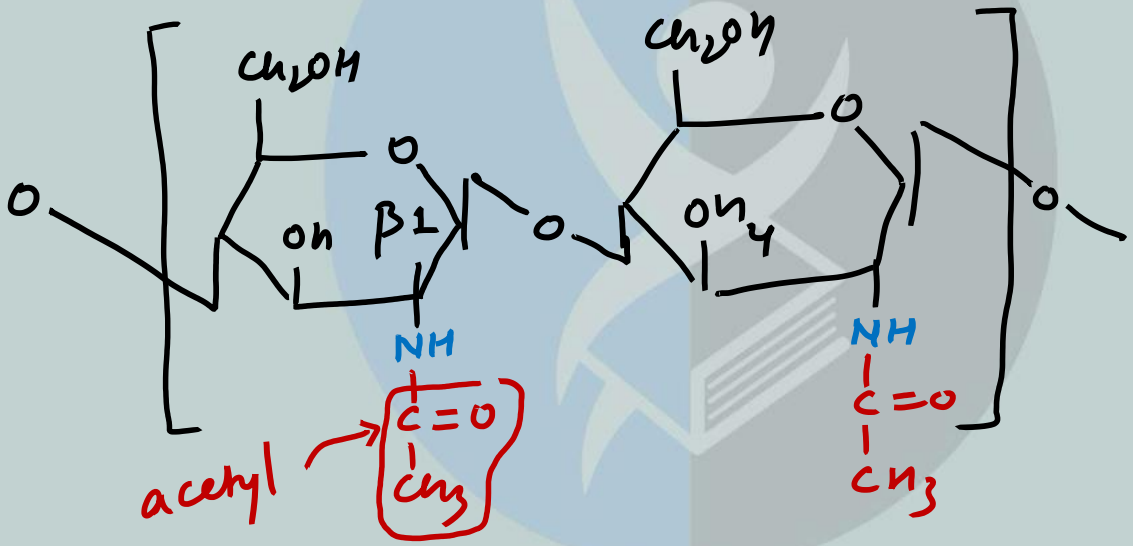
Cellulose: most abundant biomolecule

- Homopolymer of D-glucose
- β1→4 → sheet like structure
- Stabilized by interchain H-bonding
- cell wall in plants
- cellulose synthase is plasma membrane resident enzyme.
- For animals it roughage or fibre in diet not energy source
- Some animals like ruminant & termites — have symbiotic microbial association

cellulase (cellulose) → glucose → short fatty acid → energy for ruminants

Chitin: cell wall of fungus except oomycetes (cellulose)

- Homopolymer of N-acetyl-D-glucosamine (NAG)
- β 1→4, sheet like structure, interchain H-bonding



- Also present in exoskelton of insects.

Pectin : middle lamella of plant cell

- Cementing agent
- Homopolymer of D- galactouronic acid
- α 1 → 4 bonds.

Poly galactouronate = Pectate

- most hydrated sugar.

Hetero- polysaccharides : most often 1 is acidic sugar & another is basic sugar.

Mucopoly saccharide	Component of disaccharide repeats	Linkages	
Hyaluronic acid	D-glucouronic acid+ N-acetyl-D-glucasamine	β1→3	β1→4
Chondroitin sulfate	D-glucouronic acid+ N-acetyl-D-galactosamine-4-Sulfate	β1→3	β1→4
Dermatan sulfate	D-iduronic acid+ N-acetyl-D-galactosamine-4-Sulfate	α 1→3	β1→4
Kerato sulfate	D-galactose + N-acetyl-D-glucasamine-6-Sulfate	β1→4	β1→3

Heparin (Anticoagulant)

eg Peptido-glycan → NAG & NAM β1→4

Glycosamine glycans (GAG)

most of them associate with small proteins

Proteo-glycans except → Hyaluronic acid

www.ifasonline.com

thank you

Learn From India's Best Educators

India's **No.1** EdTech Company for Graduates
& Post Graduates Examination.

Download **IFAS** App Now

ANDROID IOS WINDOWS

IfAS

Harshada Sharma

Earned: ₹25,500

"As is widely recognized, IFAS stands as India's leading institute for CSIR NET examination preparation. My Personal philosophy has always revolved around helping others and I've had the pleasure of introducing the IFAS Online Course to 12 of my classmates and juniors, which in turn allowed me to earn 25,500 rupees. You too can join in and refer your friends, allowing you to earn a 5% rewards based on the fees each of your referred friends Pay"

REFER & EARN

Step – 01 Invite Friends

Share your referral code or Link with your friends.

Step – 02 Earn Cashback

On Every Purchase made using your referral code, you earn 5% instant cashback in your bank account.

Step – 03 Refer More, Earn More

Keep referring as many friends as you can and keep **Earning** cash as much as you can

Friendship is Sharing, Caring, Giving & Helping Each Other...!